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COMPARING THE INFLUENCE OF GLASS AND SILICA FILLERS ON THE CRITICAL MECHANICAL PROPERTIES OF E-GLASS CYANATE MODIFIED EPOXY LAMINATE

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ABSTRACT

Laminates that could find its way for high performance applications in Aerospace and Electronics industries requires structural rigidity besides a higher stiffness and better electrical properties. These kinds of laminates with enhanced rigidity/transmission index are required so as to get functionalized for applications like Radome, whose main requirement is to be a structurally stronger and electromagnetically transparent one, in order to transmit the EM signals with minimal attenuation loss. Such kind of materials could be a further fine tuned with an intention of upgrading their performances. These indigenous materials with additional reinforcements with different types of fillers could then be worked out for a wide spectrum of futuristic applications. By analyzing the behavior of the laminates under tensile, flexural loading and few critical electrical properties could eventually end up with a potent material that can be effectively used for signal processing applications, as in Radome. Over this perspective, laminates in cross ply configuration with 0/90/0/90 degrees as applied to a 4 plied laminates were fabricated. Cyanate ester blended with epoxy resin as matrix and E glass unidirectional fiber with 1200GSM as reinforcement with add on fillers like, Glass spheres and fumed silica in micrometer and nano meter regime were added to the laminate. Tensile and Flexural strength &their moduli were found out. It was observed that better structural responses were found for the laminate with 10% glass spheres than the ones that were made and tested with fumed Silica as filler. Addition of fumed Silica also could not be done to the same extent of glass spheres due to its rheological properties. But smaller addition of it was found to exhibit relatively better structural responses than that of Glass spheres based laminte. This is attributed to its inherent good dispersability in the resin and higher deagglomeration tendency (3), especially when added at its optimized volume fraction. Also it was proven that the type of filler and its volume fraction has an influencing role on the properties of a laminate and a precise tradeoff between the chosen parameters is required to finalize on a candidature laminate for a particular application.

KEYWORDS: Cyanate ester, Glass Spheres & Fumed Silica

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Original Article

INTRODUCTION

The epoxy resin is widely used as a matrix material for a wide variety of structural composites. It has many good properties like high stiffness, low shrinkage, good adhesion to glass/ carbon fiber, etc. But, the very factor contributing to its high stiffness and heat resistance also leads to its important shortcoming i.e., lack of toughness. From the different materials used for the modification of epoxy resins, cyanate esters are supposed to be

the best material to exhibit better thermo mechanical properties. Cyanate esters also offer a good ease of handling and processing similar to that of epoxy resin systems. Hence, blending of epoxy and cyanate ester resin continues to attract a wide research interest in order to impart improvements in fracture toughness without compromising the other mechanical and thermal properties. It is impossible to have a single material to possess all the required properties and therefore a proper balance is often required to be done between the various parameters before selecting an apt material with aggressive qualities. Since late seventies, a good number of approaches have been attempted to enhance the toughening of epoxy resin systems (6,8 and 19). Improving fracture toughness in epoxies and assisting it, by crack pinning were also some important allied work carried parallelly by many researchers (4,7,9,16,23,24 and 29). Blending Cyanate ester with Epoxy to toughen the latter, has gained widespread potential for research (14, 15, 20, 27 and 25) especially due to high structural requirements that are often required in aerospace and electronics sector (12). In this scenario, the necessity for developing such kind of materials has attracted a lot of attention in the recent past. Hence, the blend of Cyanate ester, epoxy for matrix with E Glass unidirectional 1200 GSM fiber as reinforcement are used along with fillers like glass spheres and fumed Silica, in the process of making the laminate. Though the choice of fillers is specific and performance oriented, fillers in micro and nano size as in case like glass microspheres and fumed silica are found to be more exciting due to their fundamental ability to serve as reinforcement besides their inclination to balance both structural and di electrical properties. Particle size and their volume fraction are two important criteria's that are likely to be the deciding factors in setting the trend in property patterns (11, 13, 18, 22, and 26). Quite often, laminates thus prepared were assessed for their relative structural performances with respect to two significant properties i.e., Tensile and Flexural strengths besides their moduli. (21 and 30).

In our work, 15% Cyanate ester blended epoxy resin with E Glass Unidirectional fiber were selected as matrix and reinforcement respectively for fabricating the PMC laminates with four cross plies in 0/90/0/90 orientations. Many researchers have done various analysis to understand the influence of fillers in composites (1, 2, 5, 10, 17, 25 and 28). Here, to understand the role of the fillers and to compare and contrast their influence on two critical properties oftensile and flexural strengths of the laminates, filler percentages of glass spheres and fumed silica were varied and finally got tested.

MATERIALS AND METHODS

Materials

Epoxy resin, unidirectional fibers of 1200 GSM and curing agent were purchased from Sackthi fibers, Chennai, India and Bisphenol A Cyanate ester was procured from Shangai Righton, China. Micro Glass spheres and fumed Silica in micro and nano regime respectively were imported through Sigma-Aldrich, USA (figure 1)

Figure 1: Basic Materials for Making Laminates

Figure 2: Different Cured Samples During Optimization

Trials

Tetraehyleneamine, a hardener was optimized with respect to Cyanate ester (BACY) blended Epoxy resin (DiglycidyletherofbisphenolA/DGEBA). In order to optimize the amount of hardener added in the resin, the state, form and the amount of hardener was varied. By doing good number of trails, it was observed that 25.33% of hardener addition finally led to a defect free cured mixture [as shown in fig 2]. A set resin marked with defect free state was observed visually, i.e the one without defects like pin holes, open hole and sponginess. This curing also came up with a good potting time of 20-30 minutes.

Methods and Testing

Hand lay-up procedure was adapted to fabricate laminates. Addition of curing agent (tri-ethylene tetra amine) was based on optimized value obtained out of many trails. Cyanate blending was at 15% by weight of the resin. The blend of resin and cyanate ester was stirred to ensure perfect dispersion of cyanate ester. This was further followed by the addition of the curing agent for 25.33% by weight of epoxy and was further stirred for 10 minutes. Non release agent was applied suitably on a Mylar sheet and then resin was applied with a brush. First layer of the fiber (300×300mm) was kept over the resin, and then consolidated using rollers. Similarly this procedure was redone to stack the plies in the laminates, from L1 to L7.L1 was fabricated without fillers. Care was taken to keep the fabric aligned and organized. Laminates thus formed were cured for around 8 hours. Glass microspheres of 10 %, 20% and 30% were added as fillers to the viz. L2 and L4 respectively. Fumed Silica accounting 3%, 5% and 7% as fillers were also introduced in L5 to L7. The notations are given in table 1.

Table 1: Laminate Coding Details

S.No	Name	Description
1.	EPCY – L1	4Plies + Epoxy 100g + Hardener 25.33% + Cyanate Ester 15%+ Glass Filler 0%
2.	EPCY10 F – L2	4Plies + Epoxy 100g + Hardener 25.33%+ Cyanate Ester 15% + Glass Filler 10%
3.	EPCY20 F– L3	4Plies + Epoxy 100g + Hardener 25.33%+ Cyanate Ester 15% + Glass Filler 20%

4.	EPCY30 F- L4	4Plies + Epoxy 100g + Hardener 25.33%+ Cyanate Ester 15% + Glass Filler 30%
5.	EPCY3F-L5	4Plies + Epoxy 100g + Hardener 25.33%+ Cyanate Ester 15% + Fumed Silica Filler 3%
6.	EPCY5 F=L6	4Plies + Epoxy 100g + Hardener 25.33%+ Cyanate Ester 15% + Fumed Silica Filler 5%
7.	EPCY7 F=L7	4Plies + Epoxy 100g + Hardener 25.33%+ Cyanate Ester 15% + Fumed Silica Filler 7%

Figure 3: Tensile Specimen With Glass And Silica As Fillers

Figure 4: Flexural Specimen with Glass and Silica as Fillers

As per ASTM: D638, tensile specimens [Figure 3] were prepared. A gauge section in the mid with shoulder sat the end makes up the specimens profile. For the sake of gripping the specimen while testing shoulders are provided with a larger section .The gauge section is thinner thus felicitating easy deformation and failure. For finding flexural strength, specimens [fig.4] were done by ASTMD790, standard. Transverse bending test is often employed, wherein a specimen with a rectangular cross- section is bent till fracture or yielding, by a three point flexural test method. The flexural strength captures the highest stress endured within the material at the time of rupture.

RESULTS AND DISCUSSIONS

Being an isotropic material, understanding the failure mechanism of composites is always tough and complex, the feasibility for a particular modelling is often questionable, and hence mostly the experimental approach may be the only available and acceptable solution. The observations and values thus obtained out of the experiments could establish a database for the continual quality assurance.

The tensile stress versus strain values for the composite specimen was determined during the tensile testing. It was figured out that the laminates with cyanate modified epoxy as a matrix reflected a higher tensile strength than the one made out of plain epoxy. The experimental values was found to be complimenting the theoretical facts, since it was known that cyanate ester could very well enhance cross linking density to attain the surge in the result ant values.

The higher tensile properties are due to the rigid aromatic structure and rigid triazne ring formed as a result of trimeritative reaction, owing to the blending of cyanate ester in the base resin. Besides the said primary factor, the other factors like good bonding and adhesion nature between the various elements spread across the plies of the laminate, the higher GSM of the reinforcement fibers also significantly influenced the enhanced properties.

It was also observed that the inclusion of more than 10% Glass fillers [figure 6 & table 2] in the laminates has brought down both the strength substantially. This is because of the fillers presence similar to the stress risers as found in isotropic materials. Due to the influence of induced stress during loading, the bonding in the vicinity of the fillers gets broken which ultimately starts the nucleation of micro cracks which latter snowballs into macro cracks thus resulting in pre mature failure.

Addition of Silica as fillers through an incremental mode from 3% to 7% [figure 5 & table 3] has brought down the tensile strength from gradually from 534 MPa to 205 MPa. Similar and still a steeper drop were observed, when laminates with glass spheres, as fillers were tested. Same type of pattern in the property variation was also observed when the laminates were tested for their flexural strengths.

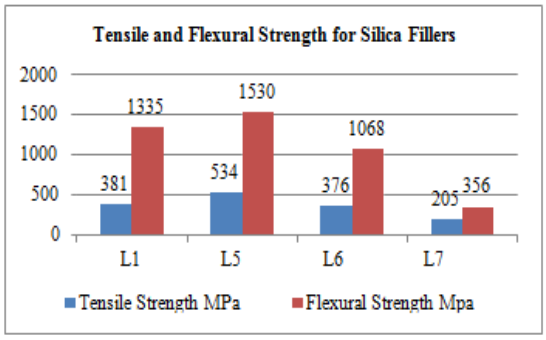

Figure 5: % of Fumed Silica Filler 0%, 3%, 5% and 7% Vs Tensile and Flexural Strength

The marginal raise in the flexural strength after cyanate loading is also seen and this is likely due to the development of a network structure between cyanate ester and epoxy matrix. Further the small variations in the said properties could also be attributed to the significant criteria's like the percentage purity of the cyanate ester and the fabrication accuracy.

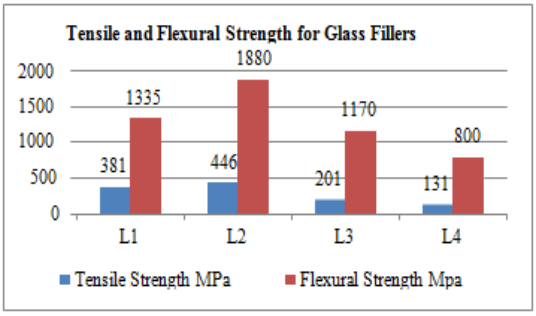

Figure 6: % of Glass Filler 0%, 10%, 20% and 30% Vs Tensile and Flexural Strength

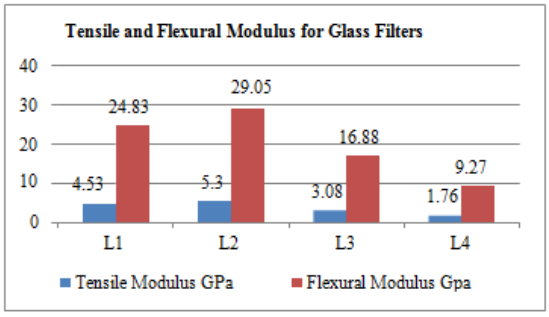

Figure 7: % of Glass Fillers 0%, 10%, 20% and 30% Vs Tensile and Flexural Modulus

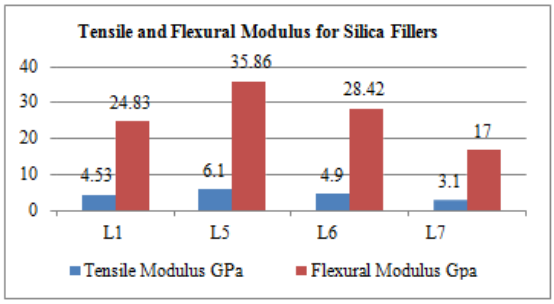

Figure 8: % of Fumed Silica filler 0%, 3%, 5% and 7% Vs Tensile and Flexural Modulus

Table 2: Tensile and Flexural Strength for Glass Fillers

Test	L1	L2	L3	L4
Tensile Strength (MPa)	381	446	201	131
Flexural Strength (Mpa)	1335	1880	1170	800

Table 3: Tensile Strength and Flexural Strength for Silica fillers

Test	L1	L5	L6	L7
Tensile Strength (MPa)	381	534	376	205
Flexural Strength (MPa)	1335	1530	1068	356

Table 4: Tensile and Flexural Modulus for Fumed Glass Fillers

Specimen Test	L1	L2	L3	L4
Tensile Modulus (GPa)	4.53	5.3	3.08	1.76
Flexural Modulus (Gpa)	24.83	29.05	16.88	9.27

Table 5: Tensile and Flexural Modulus for Fumed Silica Fillers

Specimen Test	L1	L5	L6	L7
Tensile Modulus (GPa)	4.53	6.1	4.9	3.1
Flexural Modulus (GPa)	24.83	35.86	24.82	17

CONCLUSIONS

It was observed that both tensile and flexural properties have shown an increasing trend in laminates filled with the chosen fillers when compared to their plain counterparts. But the degree of the variation with respect to the amount of the fillers added reflected the expected variation due to the generic features of the selected fillers. Glass microspheres filled laminates required 10% of its addition to develop a laminate with superior properties of tensile and flexural characteristics, wherein a mere 3% of fumed silica was found to generate an equivalent increase in the tested properties.

Fumed silica ,due to its extreme fine size acts like a colloidal agent and though added in small increments is found to be very aggressive in getting dispersed , thus effectively densifies the resin mixture ,while on getting cured. On the other hand, the coarser glass microspheres need a relatively larger volume to reflect a similar trend. Increased surface with a higher aspect ratio are two critical points in the glass fillers in enhancing the adhesion and the tested properties.

Fumed silica, basically a thixo tropic agent, due its aggressive dispersion and its tendency to increase the viscosity effectively paves for an increase in its performance through its enhanced functional properties.

Fumed silica fillers though added less in volume due to its fine insize,pins more cracks effectively than the relatively coarser glass microspheres, while being subjected to the external loads. This micro mechanism retards the rate of crack growth further assisting and helping in improving the toughness of the samples. But it has been found that after the optimum addition of fillers viz., 10 % as in glass microspheres and 3% as in case of fumed silica any further addition of fillers could not get a similar result in the laminate strength. This role reversal act of the same fillers now acting like voids after the optimum filling leads to the nucleation and growth of the cracks thus decisively reduces the measured values.

Thus, it was observed and verified about the role played by fillers like glass micro spheres and fumed silica in influencing the structural properties of the tested laminates.

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